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(54) Polymerizable liquid crystal composition and optically anisotropic film comprising the same.

(57) The present invention provides a novel polymerizable liquid crystal composition which can be used as an optical material, display material or recording material. More particularly, the present invention provides an optically anisotropic film comprising a photopolymerization product of such a polymerizable liquid crystal composition having a high orientation state fixed therein which functions to control light and is suitable for the application in the field of optoelectronics, liquid crystal display, etc. The present invention further provides a process for the preparation of such an optically anisotropic film. Moreover, the present invention provides a liquid crystal device comprising the foregoing optically anisotropic film.

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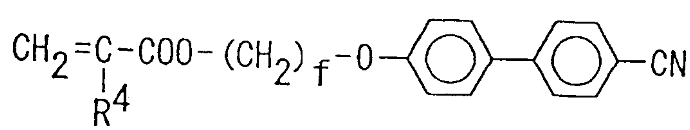
by adding a chiral compound to the polymerizable composition of the general formula (R-2) to introduce a helical structure of the mesogenic core of the liquid crystal into the optically anisotropic film.

The use of the compound of the general formula (R-2) has advantages of mechanical strength and heat resistance. However, as exemplified in the foregoing patent, a liquid crystal composition made of 80 parts by weight of a compound of the general formula (R-2) wherein R^5 is a methyl group and 20 parts by weight of a compound of the general formula (R-2) wherein R^5 is a hydrogen atom exhibits a nematic phase at a temperature as relatively higher than room temperature as between 80 and 121 °C, and an optically anisotropic film prepared from such a polymerizable liquid crystal composition disadvantageously exhibits nonuniformity of the orientation of mesogenic core of the liquid crystal, also due to inducing the undesirable heat polymerization.

The foregoing method for fixing the alignment of liquid crystal is disadvantageous in that the liquid crystalline phase of the polymerizable liquid crystal compound or polymerizable liquid crystal composition is in a relatively high temperature range, inducing photopolymerization by energy ray as well as undesirable heat polymerization that causes the loss of uniform orientation of the liquid crystal molecules. Thus, nonuniform orientation of the resultant polymer different from the desired orientation is obtained.

In this respect, it is necessary that the polymerizable liquid crystal or polymerizable liquid crystal composition has liquid crystalline temperature range in the vicinity of room temperature and that photopolymerization of the polymerizable liquid crystal or polymerizable liquid crystal composition is carried out in the vicinity of room temperature to avoid the progress of undesirable heat polymerization.

In order to solve the foregoing problem, JP-A-62-70406 discloses the use of a compound represented by the following general formula (R-1):



(R-1)

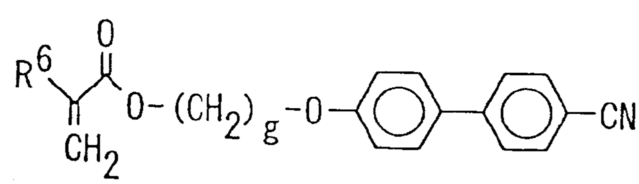
wherein f represents an integer 2, 5 or 6; and R^4 represents a hydrogen atom or a methyl group as a liquid crystal compound containing a polymerizable functional group.

The foregoing patent has no definite reference to the phase transition temperature of the liquid crystal compound used. But, the foregoing patent discloses that photopolymerization at 50 °C can provide a uniform optically anisotropic film.

However, the optically anisotropic film obtained by the photopolymerization of the compound of the general formula (R-1) is disadvantageous in that it has a low mechanical strength. The optically anisotropic film thus obtained is also disadvantageous in that when heated to around 100 °C, it loses a fixed uniform orientation, restricting its use as an optically anisotropic film.

The approach disclosed in the foregoing patent is further disadvantageous in that all the liquid crystalline acrylates exhibit a monotropically liquid crystalline phase and thus tend to undergo crystallization during photopolymerization, making it difficult to obtain an optically anisotropic film in which a uniform orientation of the mesogenic core of liquid crystal, which is fixed by photopolymerization.

Moreover, JP-A-4-227611 discloses liquid crystalline acrylate compositions containing a compound represented by the following general formula (R-3):



(R-3)

wherein R^6 represents a hydrogen atom or a methyl group; and g represents an integer 5, 6, 8, 9, 10, 11 or 12. All these compositions only exhibit a monotropically nematic phase as mentioned above. Most of these compositions immediately undergo crystallization at room temperature. These compositions exhibited a stable nematic phase, if any, for only one day at longest.

As another method for semipermanently fixing the uniform orientation of the mesogenic core of liquid crystal, there has already been known a method which comprises the use of a liquid crystalline polymer

In order to solve these problems, the inventors made extensive studies focusing on a polymerizable liquid crystal composition which exhibits a liquid crystalline phase in the vicinity of room temperature. As a result, the present invention has been worked out.

The present invention provides a polymerizable liquid crystal composition, comprising a first kind of monofunctional (meth)acrylate compound which is a (meth)acrylic ester of a cyclic alcohol, phenol or aromatic hydroxy compound with a liquid crystalline skeleton having at least two 6-membered rings as a partial structure, wherein said composition exhibits a liquid crystalline phase.

Unlike the conventional polymerizable liquid crystal compositions, the polymerizable liquid crystal composition of the present invention exhibits a liquid crystalline phase in the vicinity of room temperature. Thus, a uniform orientation can be fixed without inducing any undesirable heat polymerization during the photopolymerization in liquid crystalline state, making it possible to provide an unprecedentedly excellent optically anisotropic film.

BRIEF DESCRIPTION OF THE DRAWINGS

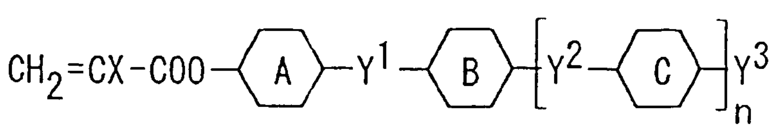
By way of example and to make the description more clear, reference is made to the accompanying drawings in which:

Fig. 1 is a graph illustrating the incident angular dependence of retardation of an optically anisotropic film according to the present invention;
Fig. 2 is a graph illustrating the incident angular dependence of retardation of another optically anisotropic film according to the present invention;
Fig. 3 is a graph illustrating the incident angular dependence of retardation of a further optically anisotropic film according to the present invention;
Fig. 4 is a diagram illustrating a glass substrate (i) used in Example 31;
Fig. 5 is a diagram illustrating a glass substrate (ii) used in Example 31;
Fig. 6 is a diagram illustrating the results of observation of a color filter for liquid crystal display device of the present invention of Example 31;
Fig. 7 is a diagram illustrating a glass substrate (iii) used in Example 32;
Fig. 8 is a diagram illustrating a glass substrate (iv) used in Example 32;
Fig. 9 is a diagram illustrating a glass substrate (v) used in Example 33;
Fig. 10 is a diagram illustrating a glass substrate (vi) used in Example 33;

DETAILED DESCRIPTION OF THE INVENTION

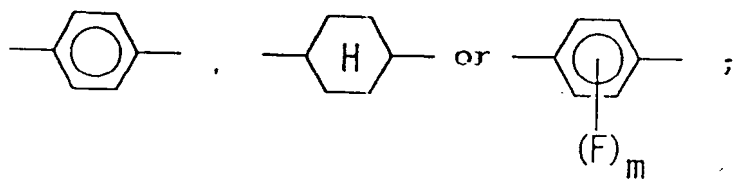
The present invention will be further described hereinafter.

The foregoing first kind of monofunctional (meth)acrylate compound to be incorporated in the polymerizable liquid crystal composition of the present invention is a compound represented by the following general formula (I):



(I)

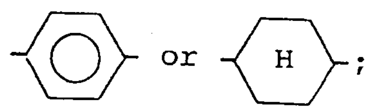
wherein X represents a hydrogen atom or a methyl group; the 6-membered rings A, B and C each independently represent



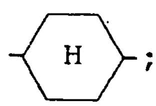
m represents an integer or 1 or 2; Y^1 and Y^2 each independently represent a single bond or -C≡C-; and Y^3 represents a halogen atom, a cyano group or a C_{1-20} alkyl or alkoxy group.

Referring further to the compound of the general formula (I) wherein n is 0, that is, a bicyclic compound, Y^3 is preferably a halogen atom, a cyano group or a C_{1-20} alkyl or alkoxy group. Particularly preferred among these compounds are the following compounds:

1. Compound wherein the 6-membered ring A represents

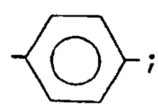


the 6-membered ring B represents



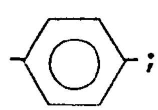
and Y^3 represents a C_{1-10} alkyl group.

2-a. Compound wherein the 6-membered rings A and B each represent



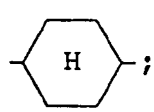
Y^1 represents a single bond; and Y^3 represents a C_{1-10} alkyl or alkoxy group or a cyano group.

2-b. Compound wherein the 6-membered rings A and B each represent

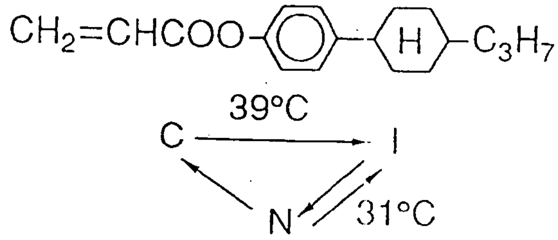


Y^1 represents -C≡C-; and Y^3 represents a C_{1-10} alkyl group.

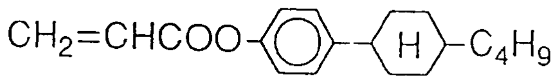
3. Compound wherein the 6-membered ring A represents



the 6-membered ring B represents

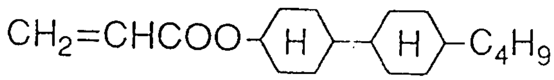


(a)



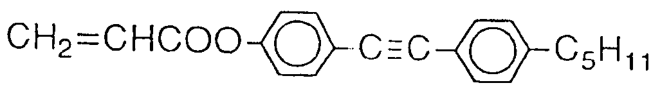
(b)

$$C \underset{}{\overset{69°C}{\rightleftarrows}} I$$



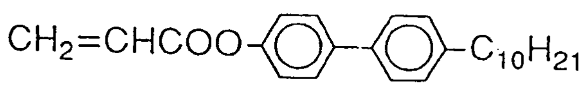
(c)

$$C \overset{60°C}{\rightleftarrows} N \overset{91°C}{\rightleftarrows} I$$



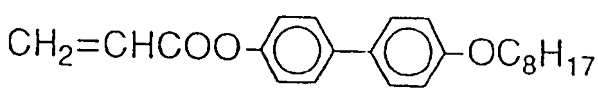
(d)

$$C \overset{54°C}{\rightleftarrows} N \overset{65°C}{\rightleftarrows} I$$



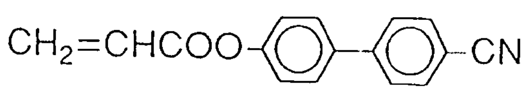
(e)

$$C \overset{53°C}{\rightleftarrows} S \overset{73°C}{\rightleftarrows} I$$



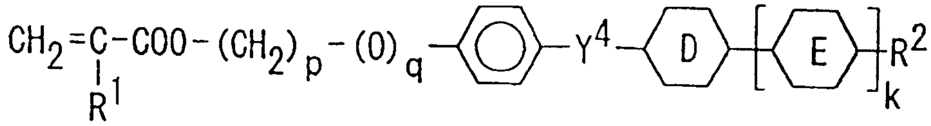
(f)

$$C \overset{65°C}{\rightleftarrows} S \overset{96°C}{\rightleftarrows} N \overset{98°C}{\rightleftarrows} I$$



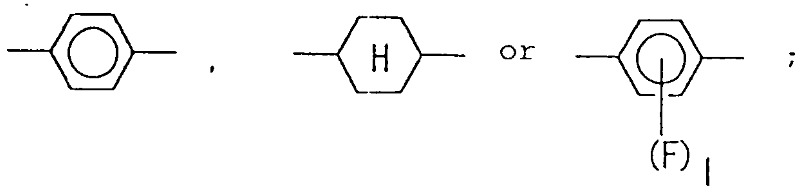
(g)

$$C \overset{103°C}{\rightleftarrows} N \overset{129°C}{\rightleftarrows} I$$



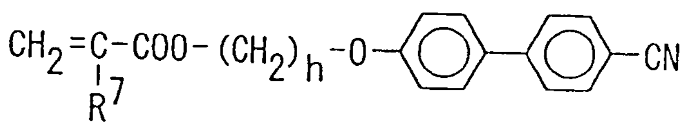
(II)

wherein R^1 represents a hydrogen atom or a methyl group; p represents an integer 2 to 12; q represents an integer 0 or 1; Y^4 represents a single bond, -COO- or -OCO-; the rings D and E each independently represent

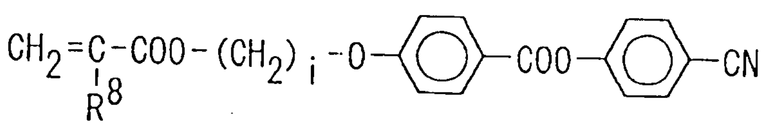


l represents an integer 1 to 4; k represents an integer 0 or 1; and R^2 represents a hydrogen atom, a halogen atom, a cyano group, a C_{1-20} alkyl group, a C_{1-20} alkoxy group, a C_{1-20} alkenyl group or a phenyl group.

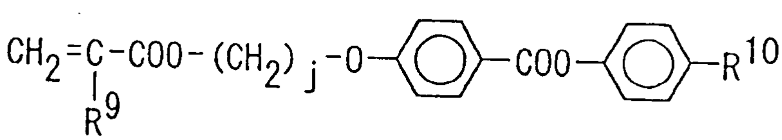
Examples of the second kind of monofunctional (meth)acrylate compound represented by the general formula (II) include compounds represented by the following general formulae (V), (VI) and (VII):



(V)



(VI)



(VII)

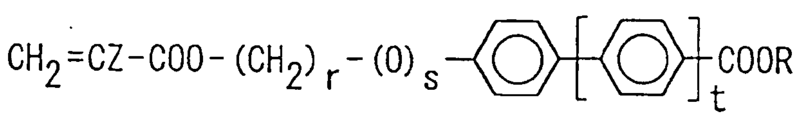
wherein R^7, R^8 and R^9 each independently represent a hydrogen atom or a methyl group; h, i and j each independently represent an integer 2 to 12; and R^{10} represents a cyano group or a C_{1-6} alkyl group, a C_{1-6} alkoxy group or a phenyl group, and compounds represented by the following general formulae (VIII) and (IX):

based on the weight of the first kind of monofunctional (meth)acrylate compound. This is because that as the content of the second kind of monofunctional (meth)acrylate compound increases the mechanical strength and heat resistivity of the resulting optically anisotropic film tend to be deteriorated.

On the other hand, if the polymerizable liquid crystal composition contains the first kind of monofunctional (meth)acrylate compound in combination with the third kind of monofunctional (meth)acrylate compound, the content of the third kind of monofunctional (meth)acrylate compound may be properly controlled depending on the degree of anisotropy of the refractive indices of the polymerizable liquid crystal composition but is preferably not less than 5 % by weight based on the weight of the polymerizable liquid crystal composition.

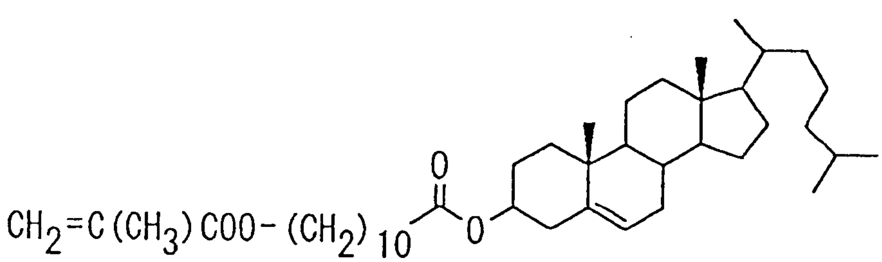
The polymerizable liquid crystal composition of the present invention may comprise a chiral compound incorporated therein besides the first, second and third kinds of monofunctional (meth)acrylate compounds for the purpose of obtaining an optically anisotropic film having a helical structure. The chiral compound employable herein doesn't have to exhibit a liquid crystallinity itself and may or may not contain a polymerizable functional group. The direction of the helix can be properly selected depending on the purpose of the optically anisotropic film. Examples of such a chiral compound include cholesterol pelargonate and cholesterol stearate containing cholesteryl group as an optically active group, "CB-15", "C-15" (available from BDH), "S1082" (available from Merck & Co.), "CM-19", "CM-20" and "CM" (available from Chisso Corporation) containing 2-methylbutyl group as an optically active agent, and "S-811" (available from Merck & Co.), "CM-21" and "CM-22" (available from Chisso Corporation) containing 1-methylheptyl group as an optically active group.

As the optically active compound containing a polymerizable function group there may be preferably used an acrylate compound or methacrylate compound containing an optically active group. Any such a compound may be used without restriction so far as it induces a chiral nematic phase in a polymerizable liquid crystal composition in the vicinity of room temperature when incorporated therein. Examples of such a polymerizable optically active compound include a compound represented by the following general formula (III):



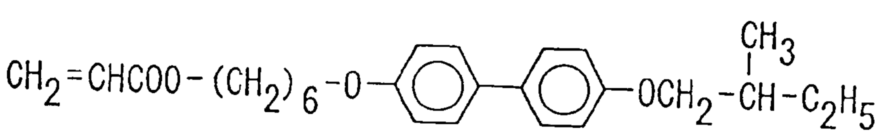
(III)

wherein Z represents a hydrogen atom or a methyl group; s represents an integer 0 or 1; r represents an integer 0 to 12 when s is 0 or an integer 1 to 12 when s is 1; t represents an integer 0 or 1; and R represents a C_{3-12} optically active hydrocarbon group, a compound represented by the general formula (X) reported by Hoyle et al., Mol. Cryst. Liquid Cryst. Inc. Nonlin. Opt., vol. 157, page 639 (1988):



(X)

and a compound represented by the general formula (XI) reported by Ringsdorf et al., Markromol. Chem., vol. 193, page 1235 (1992):



(XI)

the present invention" as used hereinafter is meant to include all these compositions unless otherwise specified.

The present invention also provides an optically anisotropic film obtained by the photopolymerization and curing of the foregoing polymerizable liquid crystal composition of the present invention.

The optically anisotropic film of the present invention as used herein means the polymer of the above-mentioned polymerizable liquid crystal composition or the polymer supported on a substrate or clamped between two substrates.

The liquid crystallinity of the polymerizable liquid crystal composition in the vicinity of room temperature makes it possible to be carried out the Photopolymerization in the vicinity of room temperature. Therefore, unlike the conventional optically anisotropic films, the optically anisotropic film of the present invention can be obtained without inducing undesirable heat polymerization during the photopolymerization in liquid crystal state so that a uniform orientation can be fixed therein to attain an excellent uniformity. In the present invention, the fixing of uniform orientation of polymerizable liquid crystal composition is achieved by photopolymerization of the liquid crystal. Thus, unlike the conventional optically anisotropic films which are made of a liquid crystalline polymer compound at glass state, the resulting optically anisotropic film shows an excellent heat resistivity. Further, the optical properties of the optically anisotropic film such as anisotropy of refractive index reflect the optical properties of the polymerizable liquid crystal composition and thus can be easily controlled by controlling the properties of the polymerizable liquid crystal composition.

The first kind of process for the preparation of an optically anisotropic film from the polymerizable liquid crystal composition of the present invention comprises irradiating the foregoing polymerizable liquid crystal composition in aligned state clamped by two sheets of substrates or carried on one sheet of substrate with energy ray such as ultraviolet ray so that it is polymerized and cured. Thus, the use of the foregoing polymerizable liquid crystal composition makes it possible to avoid undesirable heat polymerization. The first kind of preparation process will be further described hereinafter.

Firstly, the preparation process using the substrate which is treated to align the polymerizable liquid crystalline composition such as rubbing of substrate, the formation of an alignment film (organic thin film) on a substrate, or the formation of a deposition film on a substrate will be described hereinafter.

As the substrate there may be used any substrate regardless of whether it is organic or inorganic. Specific examples of organic substrate materials include polyethylene terephthalate, polycarbonate, polyimide, methyl polymethacrylate, polystyrene, polyethylene, polyvinyl chloride, polytetrafluoroethylene, polychlorotrifluoroethylene, polyacrylate, polysulfon, cellulose, and polyether ether ketone. Specific examples of inorganic substrate materials include silicon, and glass.

As the substrate employable in the present invention there may be used a rigid or flexible material. Examples of the rigid material include the foregoing polycarbonate and glass substrates. Examples of the flexible material include transparent film-like materials. The use of a polarizing film as such a substrate makes it possible to integrate the optically anisotropic film therewith. This integrated component is useful as a constituent part of liquid crystal display devices.

As the method for the alignment of the polymerizable liquid crystal composition there may be applied a low molecular liquid crystal alignment method established in the conventional technical field of liquid crystal display (as disclosed in Ekisho: Ouyouhen (Liquid Crystal: Application), Baifukan, Chapter 2) without restriction because the polymerizable liquid crystal composition consists of a low molecular liquid crystal compound.

As the method for aligning the polymerizable liquid crystal composition in a predetermined direction there may be used, e.g., a method which comprises maintaining the polymerizable liquid crystal composition in liquid crystal state clamped by or carried on a substrate which has been rubbed with cloth or the like or a substrate having an alignment film formed by oblique deposition of SiO_2. The use of a substrate which has been rubbed with cloth or the like is advantageously simple. If a proper alignment cannot be obtained even by rubbing the substrate with cloth or the like, an organic thin film such as polyimide thin film and polyvinyl alcohol thin film may be formed on the surface of the substrate by any known method before the rubbing with cloth or the like. The positive use of a polyimide thin film as used in ordinary TN or STN cells which provides a pretilt angle can advantageously provide an even accurate control of the internal structure of the optically anisotropic film.

As a method for aligning the polymerizable liquid crystal composition in horizontal to the substrate there may be used a method which comprises the formation of an organic thin film such as polyvinyl alcohol and polyimide thin films on the substrate. A method for the horizontal alignment of the liquid crystal composition without forming such an organic thin film is known. In this case, an organic thin film doesn't need to be formed on the substrate.

interposed between a first kind of transparent substrate having an electrically conductive layer and a second kind of substrate with an electrical conductivity, (2) a second step of irradiating the material with light on the first transparent substrate side with a voltage applied across the two substrates, and (3) a third step of peeling said first kind of transparent substrate and said second kind of substrate off the material.

Further, the present invention provides a third kind of preparation process a process for the preparation of an optically anisotropic film, which comprises (1) a first step of allowing a polymerizable liquid crystal composition to be interposed between a first kind of transparent substrate having an electrically conductive layer and a second kind of substrate with an electrical conductivity, (2) a second step of irradiating the material with light on the first kind of transparent substrate side with a voltage applied across the two substrates, and (3) a third step of peeling said second kind of substrate off the material.

Moreover, the present invention provides a fourth kind of preparation process for the preparation of an optically anisotropic film, which comprises (1) a first step of allowing a polymerizable liquid crystal composition to be interposed between two sheets of first kinds of transparent substrates having an electrically conductive layer, and (2) a second step of irradiating the material with light with a voltage applied across the two substrates.

The second, third and fourth kinds of preparation processes will be further described hereinafter.

As the first kind of transparent substrate to be used in the second through fourth kinds of preparation processes there may be preferably used a glass or plastic substrate having an electrically conductive layer. Specific examples of such a substrate include glass substrate with ITO, and plastic substrate with ITO. These substrates with electrical conductivity can be easily obtained by vacuum-deposition, metallization or printing on a glass or plastic substrate having no electrical conductivity. Commercially available substrates with ITO may be used.

As the second kind of substrate employable in the present invention there may be used a transparent or opaque substrate so far as it exhibits electrical conductivity itself, regardless of whether it is organic or inorganic. Specific examples of inorganic substrate materials include metals or oxides thereof, e.g., copper, gold, silver, tin, lead, iron, nickel, aluminum, ITO (indiumtin oxide). Specific examples of organic substrate materials include electrically conductive rubber, and electrically conductive plastic.

As the polymerizable liquid crystal composition there may be used the foregoing polymerizable liquid crystal composition of the present invention to avoid the induction of undesirable heat polymerization during the photopolymerization in liquid crystalline state and thus fix uniform orientation. In order to align the polymerizable liquid crystal composition in an electric field, the anisotropy of the dielectric constant of the composition is preferably positive.

In the process for the preparation of the optically anisotropic film of the present invention, the foregoing first kind of transparent substrate having an electrically conductive layer and second kind of substrate with electrical conductivity are positioned in such an arrangement that a voltage can be applied thereacross with the foregoing polymerizable liquid crystal composition interposed therebetween. As the method for allowing the polymerizable liquid crystal composition to be interposed between the two sheets of substrates there may be used the foregoing method (i) or (ii). In this process, the distance between the two sheets of substrates may be properly adjusted depending on the purpose of the optically anisotropic film thus prepared but is preferably from 0.1 to 100 μm, particularly from 0.5 to 50 μm. In this process, the alignment of the polymerizable liquid crystal composition is controlled by an electric field. Accordingly, the substrate used may or may not have the foregoing oriented film (organic thin film) or a separatable oriented film described later.

Subsequently, the laminate is irradiated with light on the first kind of transparent substrate side with a voltage applied across the two sheets of substrates. As the means of applying a voltage across the substrates there may be used a driving means as used for ordinary liquid crystal display devices. The optimum applied voltage may be properly adjusted depending on the anisotropy in the dielectric constant of the polymerizable liquid crystal composition or the distance between the two substrates but is preferably an AC voltage of not less than 0.5 V.

The photopolymerization is preferably effected by irradiating the foregoing polymerizable liquid crystal composition clamped by the two sheets of substrates with energy ray such as ultraviolet ray and electron ray. Accordingly, at least the substrate on the irradiation side must be provided with a proper transparency. The temperature at which the photopolymerization process is effected must be such that the polymerizable liquid crystal composition of the present invention can be kept in liquid crystal state. However, the photopolymerization is effected at a temperature as close to room temperature as possible to avoid undesirable heat polymerization.

Subsequently, in the second kind of preparation process, an optically anisotropic film of the present invention comprising a polymer layer alone can be easily obtained by peeling the first kind of transparent

(2) a second step of irradiating the material with light with the voltage applied across the two sheets of substrates being controlled every pixel.

In the fifth through seventh kinds of preparation processes, a polymerizable liquid crystal composition is interposed between two sheets of substrates having an electrode layer which is treated to align the liquid crystal. One of the substrates is then covered by a mask that allows only the portion corresponding to desired pixels to transmit energy ray. The material is then irradiated with energy ray with a predetermined voltage being applied across the two sheets of substrates so that the alignment determined by the predetermined voltage is fixed. The mask is then removed from the material. The material is then irradiated with energy ray on the entire surface, including the unirradiated area, with the voltage applied across the two sheets of substrates being varied depending on the portion corresponding to pixels. Thus, an optically anisotropic film having different alignment states fixed therein depending on the predetermined voltage can be prepared.

The fifth through seventh kinds of preparation processes will be further described hereinafter.

In the present invention, the first kind of transparent substrate which is treated to align the liquid crystal having an electrode layer and the second kind of substrate having an electrode layer (in the fifth and sixth kinds of preparation processes) which is treated to align the liquid crystal or two sheets of transparent substrates having an electrode layer (in the seventh kind of preparation process) are positioned in such an arrangement that a voltage can be applied across thereacross with the foregoing polymerizable liquid crystal composition being interposed therebetween.

As the transparent substrate to be used herein there should be used a substrate having an electrode layer. Specific examples of such a substrate include glass substrate with ITO, and plastic substrate with ITO. These substrates are preferably treated to align the liquid crystal. Examples of such treatments include rubbing of the surface of the substrate with cloth or the like, and oblique vacuum deposition of SiO_2. Rubbing is advantageously simple. If a proper alignment cannot be obtained even by rubbing the surface of the substrate with cloth or the like, an organic thin film such as polyimide thin film or polyvinyl alcohol thin film may be formed on the surface of the substrate by a known method before rubbing with cloth or the like. Alternatively, a separatable film which is treated to align the liquid crystal may be formed on the surface of the substrate as described later.

Subsequently, the material is irradiated with light on the transparent substrate side while the voltage applied across the two sheets of substrates being controlled every pixel. As a method for applying a voltage across the electrode layers there may be used a static driving or time shearing addressing method for use in ordinary liquid crystal display devices. The optimum applied voltage may be properly adjusted depending on the anisotropy of the dielectric constant of the polymerizable liquid crystal composition or the distance between the two substrates but is preferably an AC voltage of not less than 0.5 V.

In the preparation of the optically anisotropic film, if the alignment of the polymerizable liquid crystal composition is partially controlled by an electric field, the anisotropy of the dielectric constant of the polymerizable liquid crystal composition is preferably positive. In particular, the anisotropy $\Delta\epsilon$ in dielectric constant is preferably not less than 0.5. In order to obtain such a polymerizable liquid crystal composition, first and second kinds of monofunctional (meth)acrylate compounds containing cyano group are preferably incorporated in the composition.

The photopolymerization is preferably effected by irradiating the foregoing polymerizable liquid crystal composition clamped by the two sheets of substrates with energy ray such as ultraviolet ray and electron ray. Accordingly, at least the substrate on the irradiation side must be provided with a proper transparency. The temperature at which the photopolymerization process is effected must be such that the polymerizable liquid crystal composition of the present invention can be kept in liquid crystalline state. However, the photopolymerization is effected at a temperature as close to room temperature as possible to avoid undesirable heat polymerization.

Therefore, if the photopolymerization process is effected with the polymerizable liquid crystal composition being clamped by two sheets of substrates, at least the substrate on the irradiation side must be provided with a proper transparency.

Subsequently, one or both of the two sheets of substrates which have been used in the preparation of the optically anisotropic film are peeled off the material depending on the purpose as mentioned above.

The optical phase retardation in the optically anisotropic film of the present invention varies depending on the position corresponding to pixel but is preferably in the range of 0 to 1.8 µm, more preferably 0 to 1.2 µm. The shape and size of the portion corresponding to a pixel having a uniform retardation can be quite freely determined and can be properly selected from the group consisting of minute rectangular pixel having a side of about 60 µm, and patterns such as circle, triangle and other designs having a size of scores of centimeters depending on the purpose.

formed is then rubbed. Thus, the thin film can be used as an alignment film for providing the liquid crystal with an alignment in horizontal to the substrate. This alignment film can provide the liquid crystal with a uniform and stable orientation and provide the substrate with a good peelability with respect to the optically anisotropic film. The reason why such a good peelability can be obtained is unknown. This is possibly because that the dihydroxy compound of the general formula (IV) exhibits a very small adhesivity to a glass substrate or plastic substrate.

As the polyvinyl alcohol to be contained in the alignment film-forming composition there may be preferably used any polyvinyl alcohol which is normally solid at room temperature, regardless of its polymerization degree, to provide the liquid crystal with a stable alignment. The polymerization degree of the polyvinyl alcohol is preferably not less than 500.

Examples of the dihydroxy compound represented by the general formula (IV) to be contained in the alignment film-forming composition include 1,6-hexanediol, 1,5-hexanediol, 1,7-heptanediol, 1,2-octanediol, 1,8-octanediol, 1,9-nonanediol, 1,2-decanediol, 1,10-decanediol, 1,2-dodecanediol, 1,12-dodecanediol, 1,2-tetradecanediol, 1,14-tetradecanediol, 1,2-hexadecanediol, 1,16-hexadecanediol, and 1,4-cyclohexanedimethanol. These dihydroxy compounds represented by the general formula (IV) can be used singly or in combination.

The proportion of polyvinyl alcohol in the alignment film-forming composition is preferably in the range of 30 to 95 % by weight. If this proportion falls below this range, the dihydroxy compound of the general formula (IV) crystallizes, making it impossible to obtain a good alignment. On the other hand, if this proportion exceeds this range, there occurs a tendency to make it impossible to provide the substrate with a good peelability.

The process which comprises dissolving the alignment film-forming composition in a solvent, applying the solution to the substrate which is to be peeled, drying the material so that the solvent is dried out, and then rubbing the film formed on the substrate to obtain an alignment film will be further described hereinafter.

As the solvent for dissolving the alignment film-forming composition there may be used any solvent which is commonly recognized as a polar solvent in the art without restriction. From the standpoint of dryability, water, methanol, ethanol, or mixture thereof are particularly preferred. The concentration of the solution of the alignment film-forming composition in such a solvent is preferably in the range of 1 to 20 % by weight. The alignment film-forming composition solution may be applied to a glass substrate or plastic substrate by a method such as roll coater method, spin coater method and printing method. As the method for drying up the solvent after coating there may be used natural drying, heat drying, drying under reduced pressure or the like, singly or in combination. Whatever is the drying method, the film of alignment film-forming composition thus dried is preferably heated to a temperature of 80 to 150 °C. This heating causes the dihydroxy compound of the general formula (IV) to be uniformly dispersed in the high molecular chain of polyvinyl alcohol, making it possible to obtain a uniform film free from the deposition of dihydroxy compound. The film thus heated is then allowed to cool to room temperature. The film thus formed can then be subjected to rubbing by rayon or nylon cloth to obtain an alignment film which provides the liquid crystal with a uniform alignment and provides the substrate with a good peelability with respect to the optically anisotropic film.

The process for the preparation of an optically anisotropic film from the foregoing alignment film-forming composition will be further described hereinafter.

The alignment film made of alignment film-forming composition may be formed on only one or both of the two sheets of substrates to be used in the preparation process of the present invention. In this case, the other substrate to be opposed to the one of the two sheets of substrates may have been subjected to rubbing as it is or after the formation of an alignment film thereon. In the case where an alignment film is formed on the other substrate, any material which is commonly recognized as an alignment film-forming material in the art may be used without restriction. For example, the foregoing polyimide or polyvinyl alcohol film may be subjected to rubbing to form the desired alignment film.

After the photopolymerization, the substrate of the present invention on which an alignment film having a good peelability has been formed can be peeled off the resulting polymer to prepare an optically anisotropic film of the present invention. If the substrate is peeled off the optically anisotropic film, it can be easily effected mechanically. In this process, the substrate may be dipped in a poor solvent for both the optically anisotropic film and substrate.

Besides these processes, processes for the preparation of the optically anisotropic film according to the first, third and sixth kinds of preparation processes of the present invention at lower cost may be used. These processes will be described hereinafter.

As the third kind of transparent substrate to be used in the eighth and ninth kinds of preparation processes of the present invention there may be preferably used a substrate having transparency and optical isotropy at the same time. However, it doesn't have to exhibit orientability. Examples of such a transparent substrate include glass substrate, and plastic substrate such as polymethyl methacrylate, polyethylene, polyether sulfon, polyacrylate, amorphous polyolefin and cellulose. As another transparent substrate there may be used a polarizing film. The use of such an optically anisotropic film advantageously can reduce the trouble of separately applying the optically anisotropic film and the polarizing film in the preparation of liquid crystal display.

In the eighth kind of preparation process, the substrates which are treated to align the liquid crystal are positioned opposed to each other. In the ninth kind of preparation process, two sheets of substrates are positioned in such an arrangement that a voltage can be applied thereacross. Subsequently, the foregoing polymerizable liquid crystal composition is positioned interposed between the two sheets of substrates. In this process, the distance between the two sheets of substrates may be properly adjusted depending on the purpose of the optically anisotropic film thus prepared but is preferably in the range of 0.1 to 100 μm, particularly 0.5 to 50 μm.

In one embodiment of the eighth kind of preparation process, the polymerizable liquid crystal composition may be supported on one sheet of substrate which has been oriented. In this case, the thickness of the polymerizable liquid crystal composition is preferably in the same range as used hereinabove.

Subsequently, in the eighth kind of preparation process, the material is irradiated with light so that the polymerizable liquid crystal composition is polymerized. In the ninth kind of preparation process, the material is irradiated with light on the first kind of transparent substrate side with a voltage being applied across the two sheets of substrates to effect the polymerization thereof in the same manner as above. As a method for applying a voltage across the two sheets of substrates there may be used a driving means as commonly used in ordinary liquid crystal display devices. The optimum applied voltage may be properly adjusted depending on the anisotropy of the dielectric constant of the polymerizable liquid crystal composition or the distance between the two sheets of substrates but is preferably an AC voltage of not less than 0.5 V.

In the eighth and ninth kinds of preparation processes, the photopolymerization is preferably effected by irradiating the foregoing polymerizable liquid crystal composition clamped by the two sheets of substrates with energy ray such as ultraviolet ray and electron ray. Accordingly, at least the substrate on the irradiation side must be provided with a proper transparency. The temperature at which the photopolymerization process is effected must be such that the polymerizable liquid crystal composition of the present invention can be kept in liquid crystal state. However, the photopolymerization is effected at a temperature as close to room temperature as possible to avoid undesirable heat polymerization.

In the eighth and ninth kinds of preparation processes, one of the two sheets of substrates must be peeled off the optically anisotropic film obtained by the photopolymerization of the polymerizable liquid crystal composition. A protective layer made of a thermo-setting or photo-setting resin may be formed on the exposed surface of the optically anisotropic film to protect the surface of the optically anisotropic film.

The step of transferring the optically anisotropic film supported on the substrate thus obtained to a third kind of transparent substrate will be described hereinafter.

The term "step of transferring the optically anisotropic film" as used herein is-meant to indicate a step of applying a third kind of transparent substrate to the surface of the optically anisotropic film supported on one of the first and second kinds of substrates with an adhesive, and then peeling only the first or second kind of substrate off the material to prepare a substrate having only an optically anisotropic film supported on the third kind of transparent substrate of the present invention.

As the adhesive with which the transparent substrate is applied to the optically anisotropic film there may be used any adhesive of optical grade without restriction. For example, acrylic, epoxy, rubber and ethylene-vinyl acetate copolymer adhesives may be used.

The optically anisotropic film of the present invention prepared from various polymerizable liquid crystal compositions by respective proper preparation process can be used as phase retardation plate or alignment film for optical display devices, particularly liquid crystal display devices. An optically anisotropic film prepared by the photopolymerization and curing with a dichroic dye can be used as a polarizing plate.

The liquid crystal display device comprising such an optically anisotropic film will be further described hereinafter. Examples of the optically anisotropic film to be incorporated in the liquid crystal display device of the present invention include one comprising a polymer layer clamped by the two sheets of transparent substrates used in the preparation of the optically anisotropic film, one comprising a polymer layer supported on one sheet of transparent substrate, and one prepared by peeling at least one of the two

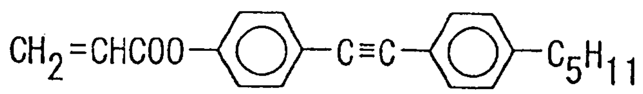
temperature from nematic phase to isotropic liquid phase was 49 °C.

EXAMPLE 3

A polymerizable liquid crystal composition (C) made of 20 parts by weight of the compound represented by formula (a) and 10 parts by weight of the compound represented by formula (c) was prepared. The composition thus obtained exhibited a nematic phase at room temperature. The phase transition temperature from nematic phase to isotropic liquid phase was 44 °C.

EXAMPLE 4

A polymerizable liquid crystal composition (D) made of 10 parts by weight of the compound represented by formula (a), 10 parts by weight of the compound represented by formula (c) and 10 parts by weight of a compound represented by formula (d):



(d)

was prepared. The composition thus obtained exhibited a nematic phase at room temperature. The phase transition temperature from nematic phase to isotropic liquid phase was 49 °C. Refractive indices at 25 °C of extraordinary light (n_e) and ordinary light (n_o) are 1.61 and 1.50, respectively.

EXAMPLE 5

A polymerizable liquid crystal composition (D-1) made of 100 parts by weight of the liquid crystal composition (D) obtained in Example 4 and 2 parts by weight of a photoinitiator "IRG-651" (available from Ciba Geigy) was obtained. A glass substrate having a rubbed polyimide-alignment film and a rubbed polycarbonate substrate were positioned with the rubbed surface thereof being opposed to each other in such an arrangement that the rubbing direction of the two substrates make an angle of 90 ° to prepare a TN structure cell having a gap of 20 µm. Into the cell was then poured the polymerizable liquid crystal composition (D-1). The cell was positioned between two sheets of polarizing plates which cross each other to confirm the orientation thereof. As a result, it was found that uniform alignment of TN structure had been obtained.

Subsequently, the cell was passed under an ultraviolet ray (metal halide lamp with 80 W) twice at a rate of 10 m/sec. at room temperature so that it was irradiated with ultraviolet ray having an energy of 350 mJ/cm^2 to cause the polymerizable liquid crystal composition to be cured. The polycarbonate substrate was then peeled off the polymer thus obtained to obtain an optically anisotropic film supported on the glass substrate. The optically anisotropic film thus obtained exhibited a high mechanical strength. The glass substrate on which the optically anisotropic film had been supported was then positioned between two sheets of polarizing plates which cross each other to confirm the orientation thereof. As a result, it was found that the optically anisotropic film had maintained uniform alignment of TN structure and had no nonuniformity even after curing by ultraviolet ray. Even when heated to a temperature of 200 °C, the optically anisotropic film maintained TN structure, showing an excellent heat resistivity.

EXAMPLE 6

An optically anisotropic film was obtained in the same manner as in Example 5 except that the polycarbonate substrate to be used as the opposing substrate was replaced by a polytetrafluoroethylene substrate. The optically anisotropic film thus obtained maintained uniform alignment of TN structure and had no nonuniformity. Similarly to Example 5, even when heated to a temperature of 200 °C, the optically anisotropic film maintained TN structure, showing an excellent heat resistivity.

the optically anisotropic film maintained 45 ° twisted nematic structure, showing an excellent heat resistivity.

EXAMPLE 10

A rubbed polytetrafluoroethylene substrate and a rubbed polycarbonate substrate were positioned with the rubbed surface thereof being opposed to each other in such an arrangement that the rubbing direction of the two substrates make an angle of 85 ° to prepare a twisted nematic structure cell having a gap of 4 μm and a twist angle of 85 °. Into the cell was then poured the same polymerizable liquid crystal composition (E-2) as used in Example 9. Subsequently, the cell was passed under an ultraviolet ray (metal halide lamp with 80 W) twice at a rate of 10 m/sec. at room temperature so that it was irradiated with ultraviolet ray having an energy of 350 mJ/cm^2 to cause the polymerizable liquid crystal composition to be cured. The polytetrafluoroethylene substrate was then peeled off the polymer thus obtained to obtain an optically anisotropic film supported on the polycarbonate substrate. The optically anisotropic film thus obtained exhibited a high mechanical strength. The polycarbonate substrate on which the optically anisotropic film had been supported was then positioned between two sheets of polarizing plates to confirm the orientation thereof. As a result, it was found that the cell had maintained uniform orientation of 85 ° twisted nematic structure and had no nonuniformity even after curing by ultraviolet ray. Even when heated to a temperature of 100 °C, the optically anisotropic film maintained 85 ° twisted nematic structure, showing an excellent heat resistivity.

EXAMPLE 11

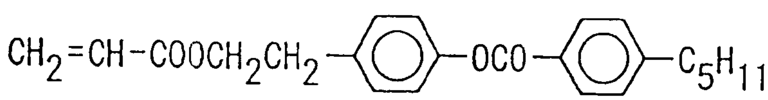
A polyvinyl alcohol was applied to a polarizing film. The polarizing film thus coated was then rubbed in the direction with which the axis of transmission of the polarizing film substrate forms an angle of 45 °. The polarizing film thus obtained and a rubbed polycarbonate substrate were positioned with the rubbed surface thereof being opposed to each other in such an arrangement that the rubbing direction of the two substrates make an angle of 85 ° to prepare a twisted nematic structure cell having a gap of 4 μm and a twist angle of 85 °. Into the cell was then poured the same polymerizable liquid crystal composition (E-2) as used in Example 9. Subsequently, the cell was passed under an ultraviolet ray (metal halide lamp with 80 W) twice at a rate of 10 m/sec. at room temperature so that it was irradiated with ultraviolet ray having an energy of 350 mJ/cm^2 to cause the polymerizable liquid crystal composition to be cured. The polycarbonate substrate was then peeled off the polymer thus obtained to obtain an optically anisotropic film supported on the polarizing film substrate. The optically anisotropic film thus obtained served as a uniform ellipsoidal polarizing plate. Even when heated to a temperature of 100 °C, the optically anisotropic film maintained 85 ° twisted nematic structure, showing an excellent heat resistivity.

EXAMPLE 12

A polyvinyl alcohol was applied to a polarizing film substrate. The polarizing film thus coated was then rubbed in the direction with which the axis of transmission of the polarizing film substrate forms an angle of 30 °. The polarizing film thus obtained and a rubbed polycarbonate substrate were positioned with the rubbed surface thereof being opposed to each other with a gap of 10.0 μm in such an arrangement that the rubbing direction of the two substrates make an angle of 240 ° with right-handed direction to prepare a twisted nematic structure cell. Into the cell was then poured the same polymerizable liquid crystal composition (E-1) as used in Example 8. Subsequently, the cell was then irradiated with ultraviolet ray of 200 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) on the polycarbonate substrate side to cause the polymerizable liquid crystal composition to be cured. The polycarbonate substrate was then peeled off the polymer thus obtained to obtain an optically anisotropic film having a 240 ° of right-handed helical structure supported on the polarizing film substrate.

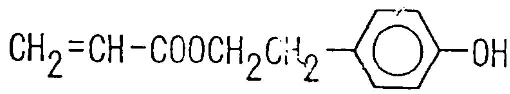
The nonpolymerizable liquid crystal composition (M) obtained in Example 8 was then poured into an STN cell made of two sheets of glass substrates with a transparent electrode having a rubbed polyimide-alignment film with a cell gap of 6.2 μm and a twist angle of 240 ° of the left-handed direction. The STN cell was then clamped between a sheet of polarizing film and the polarizing film on which the optically anisotropic film had been supported to prepare a liquid crystal display device. In this arrangement, the STN cell was brought into contact with the optically anisotropic film supported on the polarizing film, and the angle made by the axis of transmission of the polarizing film and the rubbing direction of the glass substrate of the STN cell was the same as in Example 8. When a voltage was applied across the

REFERENCE EXAMPLE 1: Synthesis of Compound (I)



(I)

1st stage: synthesis of alcohol derivative (I-a)



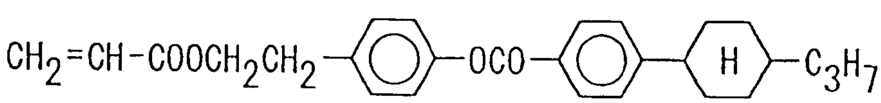
(I-a)

10.00 g of 2-(hydroxyphenyl)ethyl alcohol, 20.75 g of acrylic acid, and 3.00 g of p-toluenesulfonic acid were dissolved in 150 mℓ of benzene. The solution was then heated to reflux while water content thus produced was being separated therefrom by means of a Dean-Stark water separator for 10 hours. After the completion of reaction, the reaction product was allowed to cool to room temperature. The reaction solution was then washed with water. Benzene was then distilled off under reduced pressure to obtain 12.6 of a crude product. The crude product was then purified by silica gel column chromatography (1 : 1 mixture of ethyl acetate and n-hexane; Rf = 0.53) to obtain 10.1 g of an alcohol derivative (I-a).

2nd stage: synthesis of Compound (I)

To 5.00 g of p-n-pentylbenzoate were added 10 mℓ of thionyl chloride and 0.01 g of dimethylformamide. The mixture was then stirred at room temperature for 10 minutes. Unreacted thionyl chloride was distilled off under reduced pressure. To the residue was then added 30 mℓ of methylene chloride. The solution was then added dropwise to a solution of 5.00 g of the alcohol derivative (I-a) obtained in the 1st stage and 6.10 g of triethylamine in 70 mℓ of methylene chloride while the temperature thereof was being kept to not higher than 5 °C in 10 minutes. The mixture was then stirred at room temperature for 30 minutes. After the completion of reaction, the resulting reaction solution was extracted with 150 mℓ of methylene chloride. The resulting organic phase was then washed with water. The organic solvent was then distilled off under reduced pressure to obtain 9.10 g of a crude product. The crude product was then purified by column chromatography (1 : 5 mixture of ethyl acetate and n-hexane; Rf = 0.44). The product was then recrystallized from 35 mℓ of ethanol to obtain 6.25 g of Compound (I). Compound (I) exhibited an isotropic liquid phase at room temperature (25 °C).

REFERENCE EXAMPLE 2: Synthesis of Compound (m)



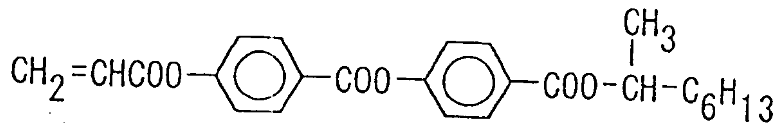
(m)

A solution of 6.90 g of p-(trans-4-n-propylcyclohexyl)benzoic chloride in 30 mℓ of methylene chloride was added dropwise to a solution of 5.00 g of the alcohol derivative (I-a) and 6.10 g of triethylamine in 70 mℓ of methylene chloride while the temperature thereof was being kept to not higher than 0 °C in 10 minutes. The mixture was then stirred at room temperature for 120 minutes. After the completion of reaction, the resulting reaction solution was extracted with 300 mℓ of methylene chloride. The resulting organic phase was then washed with water. The organic solvent was then distilled off under reduced pressure to obtain 11.10 g of a crude product. The crude product was then purified by column chromatography (1 : 10 mixture of ethyl acetate and n-hexane; Rf = 0.21). The product was then recrystallized from 30 mℓ of ethanol to obtain 5.60 g of Compound (m). Compound (m) exhibited a crystal phase at room temperature (25 °C). Compound (m) was shifted to enantiotropically nematic phase at a temperature of 68

polyimide-alignment film faced inward. The polymerizable liquid crystal composition (F-2) obtained in Example 17 was provided interposed between the two sheets of glass substrates. In this arrangement, the rubbing direction of the substrates made an angle of 90 ° counterclockwise. The polymerizable liquid crystal composition (F-2) clamped by the two sheets of glass substrates was placed between two sheets of polarizing plates which cross each other to observe the alignment thereof. As a result, it was confirmed that the polymerizable liquid crystal composition had a uniform twisted nematic alignment. The polymerizable liquid crystal composition (F-2) was then irradiated with ultraviolet ray of 160 mJ/cm^2 from a UV lamp (UVGL-25 available from UVP) to effect the photopolymerization thereof. As a result, an optically anisotropic film clamped by the two sheets of glass substrates was obtained. The optically anisotropic film thus obtained was kept at a temperature of 150 °C for 10 minutes, and then allowed to cool to room temperature. The two sheets of glass substrates were then peeled off the optically anisotropic film to obtain an independent optically anisotropic film. The optically anisotropic film thus obtained was then placed between two sheets of polarizing plates which cross each other to observe the orientation thereof. As a result, it was confirmed that the uniform twisted nematic alignment established before photopolymerization had been fixed by photopolymerization. Even when stored at a temperature of 150 °C for 34 hours, the optically anisotropic film maintained the uniform twisted nematic alignment, showing an excellent heat resistivity.

EXAMPLE 19

A polymerizable liquid crystal composition (E-3) made of 99 parts by weight of the polymerizable liquid crystal composition (E) obtained in Example 7, 1 part by weight of the photopolymerization initiator "IRG-651" (available from Ciba Geigy), and 1.25 parts by weight of a compound represented by formula (III-b):



(III-b)

wherein the absolute configuration of asymmetric carbon atom is the S configuration was prepared. The polymerizable liquid crystal composition (E-3) was measured for pitch. As a result, the pitch was 8.2 μm with left-handed direction, proving that a chiral nematic liquid crystalline composition had been obtained.

EXAMPLE 20

Two sheets of glass substrates having a polyimide-alignment film formed thereon which had been rubbed were positioned opposed to each other with a gap of 6 μm in such an arrangement that the polyimide-alignment film faced inward. The polymerizable liquid crystal composition (E-3) obtained in Example 19 was provided interposed between the two sheets of glass substrates. In this arrangement, the rubbing direction of the substrates made an angle of 270 ° with left-handed direction. The polymerizable liquid crystal composition (E-3) clamped by the two sheets of glass substrates was placed between two sheets of polarizing plates which cross each other to observe the orientation thereof. As a result, it was confirmed that the polymerizable liquid crystal composition had a uniform supertwisted nematic alignment. The polymerizable liquid crystal composition (E-3) was then irradiated with ultraviolet ray of 160 mJ/cm^2 from a UV lamp (UVGL-25 available from UVP) to effect the photopolymerization thereof. As a result, an optically anisotropic film clamped by the two sheets of glass substrates was obtained. The optically anisotropic film thus obtained was kept at a temperature of 150 °C for 10 minutes, and then allowed to cool to room temperature. The two sheets of glass substrates were then peeled off the optically anisotropic film to obtain an independent optically anisotropic film. The optically anisotropic film thus obtained was then placed between two sheets of polarizing plates which cross each other to observe the alignment thereof. As a result, it was confirmed that the uniform supertwisted nematic alignment established before photopolymerization had been maintained, showing an excellent heat resistivity.

provided interposed between the two sheets of glass substrates in the same manner as in Example 22. The polymerizable liquid crystal composition clamped by the two sheets of glass substrates was then observed under a polarizing microscope. As a result, no defects were observed, proving that the polymerizable liquid crystal composition had a uniform homogeneous alignment. The polymerizable liquid crystal composition clamped by the two sheets of glass substrates was then irradiated with ultraviolet ray of 160 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) at room temperature so that the polymerizable liquid crystal composition was subjected to photopolymerization for curing. One of the two sheets of glass substrates was then peeled off the polymer thus obtained to obtain an optically anisotropic film. The optically anisotropic film thus obtained was then observed under a polarizing microscope. As a result, it was found that the optically anisotropic film had no defects and a uniform homogeneous orientation established before photopolymerization had been completely fixed therein. The optically anisotropic film was measured for dependence of retardation on angle of incidence by means of a He-Ne laser. The results are set forth in Fig. 2.

The angle of incidence as defined herein indicates the angle of incident light from the normal line of the substrate within a plane formed by the rubbing direction and the normal line of the substrate. Fig. 2 shows that a homogeneous orientation is fixed in the optically anisotropic film. Even when stored at a temperature of 120 °C, the optically anisotropic film maintained the homogeneous alignment, showing no problem of heat resistivity.

EXAMPLE 24

A 0.1 wt.% ethanol solution of egg yolk lecithin was applied on a glass substrate to form a vertically-alignment film. A polyimide alignment agent "Al-1254" (available from Japan Synthetic Rubber Co., Ltd.) was applied on a glass substrate, dried at a temperature of 120 °C for 1 hour to form a polyimide-alignment film, and then rubbed with rayon cloth. The glass substrate having a vertically-alignment film formed thereon and the rubbed glass substrate were then positioned opposed to each other with a gap of 9 µm. The polymerizable liquid crystal composition (E-2) was then provided interposed between the two sheets of glass substrates in the same manner as in Example 22. The polymerizable liquid crystal composition clamped by the two sheets of glass substrates was placed interposed between two sheets of polarizing plates which cross each other for observation. As a result, no defects were observed, proving that the polymerizable liquid crystal composition had a uniform hybrid orientation. The polymerizable liquid crystal composition clamped by the two sheets of glass substrates was then irradiated with ultraviolet ray of 160 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) at room temperature so that the polymerizable liquid crystal composition was subjected to photopolymerization for curing. The glass substrate having a vertically-oriented film formed thereon was then peeled off the polymer thus obtained to obtain an optically anisotropic film. The optically anisotropic film thus obtained was then placed interposed between two sheets of polarizing plates which cross each other for observation. As a result, it was found that a uniform hybrid orientation established before photopolymerization had been completely fixed in the optically anisotropic film. The optically anisotropic film was measured for dependence of retardation on angle of incidence by means of a He-Ne laser. The results are set forth in Fig. 3.

The angle of incidence as defined herein indicates the angle of incident light from the normal line of the substrate within a plane formed by the rubbing direction and the normal line of the substrate. Fig. 3 shows that a hybrid alignment is fixed in the optically anisotropic film. Even when stored at a temperature of 120 °C, the optically anisotropic film maintained the hybrid alignment, showing no problem of heat resistivity.

EXAMPLE 25

A polycarbonate substrate and a polytetrafluoroethylene substrate which had both been rubbed with rayon cloth were positioned opposed to each other with a gap of 8 µm in such an arrangement that the rubbing direction thereof made an angle of 180 °. The polymerizable liquid crystal composition (E-2) was then provided interposed between the two sheets of substrates in the same manner as in Example 22. The polymerizable liquid crystal composition clamped by the polycarbonate substrate and the polytetrafluoroethylene substrate was irradiated with ultraviolet ray of 350 mJ/cm^2 from an ultraviolet lamp (metal halide lamp with 80 W) at room temperature on the polycarbonate substrate side so that it was subjected to photopolymerization for curing. The polytetrafluoroethylene substrate was then peeled off the polymer thus obtained to obtain an optically anisotropic film. The optically anisotropic film thus obtained was then observed for the conditions of the polymer under a polarizing microscope. As a result, it was found that the optically anisotropic film had no defects and had a uniform homogeneous alignment fixed therein. Even

EXAMPLE 28

A sheet of glass substrate with an ITO transparent electrode on which a 0.1 wt.% ethanol solution of egg yolk lecithin as a release agent had been applied and dried and another sheet of glass substrate with an ITO transparent electrode were positioned opposed to each other with a gap of 10 μm in such an arrangement that the ITO surfaces thereof faced inward. The polymerizable liquid crystal composition (G-1) prepared in Example 27 was then provided interposed between the two sheets of glass substrates. The polymerizable liquid crystal composition clamped by the two sheets of glass substrates with an ITO transparent electrode was then observed under a polarizing microscope. As a result, it was confirmed that the polymerizable liquid crystal composition had a nonuniform alignment, i.e., random alignment. A 1 KHz sinusoidal wave having 50 Vrms was applied across the two ITO electrodes by which the randomly-aligned polymerizable liquid crystal composition had been clamped. It was confirmed by a conoscope that the polymerizable liquid crystal composition had been vertically aligned under these conditions. While being vertically aligned under the application of a voltage, the polymerizable liquid crystal composition was irradiated with ultraviolet ray of 160 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) at room temperature so that the polymerizable liquid crystal composition was subjected to photopolymerization for curing. The glass substrate coated with egg yolk lecithin was then peeled off the polymerizable liquid crystal composition to obtain an optically anisotropic film supported on the other glass substrate with an ITO transparent electrode. The optically anisotropic film thus obtained was then observed by a conoscope. As a result, it was confirmed that the vertical orientation established before polymerization had been fixed in the polymerizable liquid crystal composition. Further, the optically anisotropic film was placed interposed between two sheets of polarizing plates which cross each other for observation. As a result, the optically anisotropic film showed a uniformly dark view, proving that a uniform vertical alignment was obtained. Thus, it was made obvious that an optically anisotropic film having a thickwise refractive index greater than inplace refractive index and an excellent uniformity was obtained. Even when stored at a temperature of 120 °C, the optically anisotropic film maintained the uniform vertical orientation, showing no problem of heat resistivity.

EXAMPLE 29

The polymerizable liquid crystal composition was subjected to photopolymerization for curing in the same manner as in Example 28 except that an aluminum plate having a thickness of 1 mm was used instead of the glass substrate with an ITO transparent electrode. The aluminum plate was then peeled off the polymerizable liquid crystal composition to obtain an optically anisotropic film supported on the glass substrate with an ITO substrate. The optically anisotropic film thus obtained was then observed by a conoscope. As a result, it was confirmed that the vertical orientation established before polymerization had been fixed as it is. The optically anisotropic film was placed between two sheets of polarizing plates which cross each other for observation. As a result, the optically anisotropic film showed a uniformly dark view, proving that a uniform vertical alignment was obtained. Thus, it was made obvious that an optically anisotropic film having a thickwise refractive index greater than inplace refractive index and an excellent uniformity was obtained. Even when stored at a temperature of 120 °C, the optically anisotropic film maintained the uniform vertical alignment, showing no problem of heat resistivity.

EXAMPLE 30

A sheet of glass substrate with an ITO transparent electrode on which a 0.1 wt.% ethanol solution of egg yolk lecithin as a release agent had been applied and dried and another sheet of glass substrate with an ITO transparent electrode were positioned opposed to each other with a gap of 20 μm in such an arrangement that the ITO surfaces thereof faced inward. The polymerizable liquid crystal composition (G-1) prepared in Example 27 was then provided interposed between the two sheets of glass substrates. The polymerizable liquid crystal composition clamped by the two sheets of glass substrates with an ITO transparent electrode was then observed under a polarizing microscope. As a result, it was confirmed that the polymerizable liquid crystal composition had a nonuniform orientation, i.e., random orientation. A 1 KHz sinusoidal wave having 100 Vrms was applied across the two ITO electrodes by which the randomly-oriented polymerizable liquid crystal composition had been clamped. It was confirmed by a conoscope that the polymerizable liquid crystal composition had been vertically aligned under these conditions. While being vertically aligned under the application of a voltage, the polymerizable liquid crystal composition was irradiated with ultraviolet ray of 160 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) at room

EXAMPLE 32

A polyimide orienting agent "AL-1254" was spin-coated onto a 25 mm x 30 mm glass substrate (iii) having electrode layers (A'), (B') and (C') as ITO transparent electrode layers as shown in Fig. 7. The substrate was then stored at a temperature of 180 °C for 80 minutes to form a polyimide film thereon. The polyimide film was then rubbed in the direction shown in Fig. 4 to prepare an oriented glass substrate (iii-R). The polyimide alignment agent "AL-1254" was spin-coated onto a glass substrate (iv) of the same size as the glass substrate (iii) having an ITO transparent electrode layer on the entire surface thereof as shown in Fig. 8. The substrate was then stored at a temperature of 180 °C for 80 minutes to form a polyimide film thereon. The polyimide film was then rubbed in the direction shown in Fig. 8 to prepare a glass substrate which is treated to align the liquid crystals (iv-R). The glass substrate (iii-R) and the glass substrate (iv-R) were positioned opposed to each other in such an arrangement that the rubbed surfaces thereof faced each other. A nematic liquid crystal composition "PN-019" (available from Rodic Co., Ltd.) having a refractive index anisotropy of 0.189 and a dielectric constant anisotropy of 7.2 was provided interposed between the two sheets of glass substrates. In this arrangement, the gap between the two sheets of glass substrates and the angle made by the rubbing direction of the glass substrates were determined to 5.3 μm and 90 °, respectively. Thus, a twisted nematic liquid crystal cell was prepared. The optically anisotropic film prepared in Example 31 was then superimposed on the twisted nematic liquid crystal cell. The laminate was then placed between two sheets of polarizing films whose axis of polarization run in parallel to each other. In this arrangement, the axis of polarization of the two sheets of polarizing films made an angle of 45 ° with respect to the optical axis (rubbing direction) of the optically anisotropic film. Further, the respective rubbing direction of the two sheets of substrates constituting the twisted nematic liquid crystal cell is parallel or perpendicular to the axis of polarization of the polarizing film. In the laminate, the portion on the optically anisotropic film which exhibits an interference color of red faced the electrode layer (A') of the liquid crystal cell, the portion on the optically anisotropic film which exhibits an interference color of green faced the electrode layer (B') of the liquid crystal cell, and the portion on the optically anisotropic film which exhibits an interference color of blue faced the electrode layer (C') of the liquid crystal cell. The liquid crystal display device thus prepared exhibited sharp colors of red, green and blue at the electrode layers (A'), (B') and (C'), respectively, when no voltage was applied across the electrodes. When a voltage was applied across the electrodes, the liquid crystal display device exhibited sharp colors of green, red and yellow at the electrode layers (A'), (B') and (C'), respectively.

EXAMPLE 33

A polymerizable liquid crystal composition (H) made of 80 parts by weight of the same nematic liquid crystal composition "PN-019" as used in Example 32, 13.6 parts by weight of a caprolacton-modified neopentylglycol diacrylate hydroxypivalate "HX-220" (available from Nippon Kayaku Co., Ltd.), 6 parts by weight of lauryl acrylate "L-A" (available from Kyoei Yushi Kagaku Kogyo K.K.), and 0.4 parts by weight of a photopolymerization initiator "IRG-651" (available from Ciba Geigy) was prepared. A 25 mm x 30 mm glass substrate (V) having electrode layers (A"), (B") and (C") as ITO transparent electrodes as shown in Fig. 9 and a glass substrate of the same size as the glass substrate (v) having an ITO transparent electrode on the entire surface thereof as shown in Fig. 10 were prepared. The glass substrate (v) and the glass substrate (vi) were positioned opposed to each other. The polymerizable liquid crystal composition (H) was then provided interposed between the two sheets of glass substrates. In this arrangement, the gap between the two sheets of glass substrates was determined to 12 μm. The polymerizable liquid crystal composition clamped by the two sheets of glass substrates was then irradiated with ultraviolet ray of 500 mJ/cm^2 from a metal halide lamp with 80 W so that it was subjected to polymerization to prepare a liquid crystal cell having a light adjusting layer made of transparent solid substance and liquid crystal material between the two sheets of substrates. The optically anisotropic film prepared in Example 31 was then superimposed on the liquid crystal cell. The laminate was then placed between two sheets of polarizing films whose axis of polarization cross each other. In this arrangement, the optical axis (rubbing direction) of the optically anisotropic film made an angle of 45 ° with respect to the axis of polarization of the polarizing films. In the laminate, the portion on the optically anisotropic film which exhibits an interference color of red faced the electrode layer (A") of the liquid crystal cell, the portion on the optically anisotropic film which exhibits an interference color of green faced the electrode layer (B") of the liquid crystal cell, and the portion on the optically anisotropic film which exhibits an interference color of blue faced the electrode layer (C") of the liquid crystal cell. The liquid crystal display device thus prepared exhibited cloudy (white) at the electrode layers (A"), (B") and (C") when no voltage was applied across the electrodes. When a voltage was applied

mechanical force to obtain an optically anisotropic film supported on the glass substrate (ii). In this process, the glass substrate (i) could be easily peeled off the material, and there were observed no components of the optically anisotropic film attached thereto. When peeled off the optically anisotropic film, the glass substrate (i) didn't give any damage such as mark and crack to the optically anisotropic film. Thus, 10 sheets of the optically anisotropic films were prepared. With all these sheets of the optically anisotropic films, peeling could be effected with a good reproducibility. As a result, optically anisotropic films free of mark or crack could be obtained. Even when kept at a temperature of 120 °C, the optically anisotropic film maintained the uniform orientation, showing no problem of heat resistivity.

COMPARATIVE EXAMPLE 1

3.0 g of a polyvinyl alcohol was dissolved in 100 g of water to prepare a solution. The solution thus obtained was then spin-coated onto a glass substrate. The glass substrate was then allowed to cool to room temperature. The glass substrate was then rubbed to obtain a glass substrate (iii) having a polyvinyl alcohol-oriented film formed thereon. The glass substrate (iii) and the glass substrate (ii) prepared in Example 34 were positioned opposed to each other in such an arrangement that the rubbed surfaces thereof faced each other. The polymerizable liquid crystal composition (E-5) prepared in Example 34 was then provided interposed between the two sheets of glass substrates. In this arrangement, the gap between the two sheets of glass substrates and the angle made by the rubbing direction thereof were determined to 8 μm and 180 °, respectively. The polymerizable liquid crystal composition clamped by two sheets of glass substrates was placed between two sheets of polarizing plates for observation. As a result, it was confirmed that a uniform uniaxial alignment (homogeneous alignment) had been obtained. The polymerizable liquid crystal composition was irradiated with ultraviolet ray of 160 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) at room temperature so that the polymerizable liquid crystal composition was subjected to photopolymerization for curing. After photopolymerization, the substrates by which the polymer had been clamped were placed between two sheets of polarizing plates for observation. As a result, it was confirmed that the uniform uniaxial alignment (homogeneous alignment) established before photopolymerization had been fixed in the polymer, proving that an optically anisotropic film having an excellent uniformity had been obtained. The glass substrate (iii) was then peeled off the optically anisotropic film by a mechanical force in an attempt to obtain an optically anisotropic film supported on the glass substrate (ii). However, the glass substrate could not be smoothly peeled off the optically anisotropic film, and there were observed some components of the optically anisotropic film attached thereto. When peeled off the optically anisotropic film, it was observed that the glass substrate (ii) gave some damage such as mark and crack to the optically anisotropic film. Thus, 10 sheets of the optically anisotropic films were prepared. All these sheets of the optically anisotropic films showed no problem of heat resistivity. However, 8 of the ten sheets of the optically anisotropic films wore observed to suffer from damage such as mark and damage, showing a poor yield in the production.

COMPARATIVE EXAMPLE 2

The glass substrate (iii) prepared in Comparative Example 1 and the glass substrate (ii) prepared in Example 34 were positioned opposed to each other in such an arrangement that the rubbed surfaces thereof faced each other. The polymerizable liquid crystal composition (E-5) prepared in Example 34 was then provided interposed between the two sheets of glass substrates. In this arrangement, the gap between the two sheets of glass substrates and the angle made by the rubbing direction thereof were determined to 8 μm and 85 °, respectively. The polymerizable liquid crystal composition clamped by two sheets of glass substrates was placed between two sheets of polarizing plates for observation. As a result, it was confirmed that a uniform twisted nematic orientation had been obtained. The polymerizable liquid crystal composition was irradiated with ultraviolet ray of 160 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) at room temperature so that the polymerizable liquid crystal composition was subjected to photopolymerization for curing. After photopolymerization, the cured product was placed between two sheets of polarizing plates which cross each other for observation. As a result, it was confirmed that the uniform twisted nematic alignment established before photopolymerization had been fixed in the polymer, proving that an optically anisotropic film having an excellent uniformity had been obtained. The glass substrate (iii) was then peeled off the optically anisotropic film by a mechanical force in an attempt to obtain an optically anisotropic film supported on the glass substrate (ii). However, the glass substrate (iii) could not be smoothly peeled off the optically anisotropic film, and there were observed some components of the optically anisotropic film attached thereto. When peeled oft the optically anisotropic film, it was observed that the glass substrate (iii)

The optically anisotropic film thus obtained was then observed by a conoscope. As a result, it was confirmed that the vertical orientation established before polymerization had been completely fixed in the polymerizable liquid crystal composition. Further, the optically anisotropic film was placed interposed between two sheets of polarizing plates which cross each other for observation. As a result, the optically anisotropic film showed a uniformly dark view, proving that a uniform vertical orientation was obtained.

The optically anisotropic film was then processed in the same manner as in Example 36 to transfer the optically anisotropic film to the glass substrate.

EXAMPLE 39

The nonpolymerizable liquid crystal composition (M) as used in Example 8 was poured into an STN cell with a cell gap of 6.2 µm and a twist angle of 240 ° counterclockwise made of two sheets of glass substrates with a transparent electrode having a rubbed polyimide-alignment film to prepare an STN liquid crystal cell.

An optically anisotropic film supported on a rubbed polycarbonate substrate was prepared in the same manner as in Example 36. The optically anisotropic film thus obtained was then thinly coated with an ultraviolet-curing adhesive "3052B" (available from Tree Bond). The optically anisotropic film was then slowly placed on the glass substrate of the foregoing STN liquid crystal cell with the coated surface thereof faced downward. In this arrangement, the rubbing direction of the polycarbonate substrate and the rubbing direction of the glass substrate on the side of the STN liquid crystal cell which is not brought into contact with the ultraviolet-curing adhesive made right angle. The laminate was then irradiated with ultraviolet ray of 300 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) on the polycarbonate substrate side so that the ultraviolet-curing adhesive was cured to bond the optically anisotropic film to the glass substrate of the STN liquid crystal cell. The laminate was kept at a temperature of 150 °C for 5 minutes, and then allowed to cool to room temperature. The polycarbonate substrate was then peeled off the optically anisotropic film to prepare a liquid crystal cell having an optically anisotropic film supported on the other glass substrate of the STN liquid crystal cell. The liquid crystal cell was clamped by two sheets of polarizing plates which cross each other to prepare a liquid crystal display device. When a voltage was applied across the transparent electrodes of the liquid crystal display device, a uniform black-and-white display was provided over a wide range. The liquid crystal display device also exhibited excellent viewing angle properties.

EXAMPLE 40

An optically anisotropic film supported on a rubbed polycarbonate substrate was prepared in the same manner as in Example 36. The optically anisotropic film thus obtained was then thinly coated with an ultraviolet-curing adhesive "3052B" (available from Tree Bond). The optically anisotropic film was then slowly placed on a polarizing film with the coated surface thereof faced downward. In this arrangement, the rubbing direction of the polycarbonate substrate and the axis of transmission of the polarizing film substrate made an angle of 30 °. The laminate was then irradiated with ultraviolet ray of 300 mJ/cm^2 from an ultraviolet lamp (UVGL-25 available from UVP) on the polycarbonate substrate side so that the ultraviolet-curing adhesive was cured to bond the optically anisotropic film to the polarizing film substrate. The laminate was kept at a temperature of 100 °C for 30 minutes, and then allowed to cool to room temperature. The polycarbonate substrate was then peeled off the optically anisotropic film to prepare an optically anisotropic film supported on the polarizing film substrate. The optically anisotropic film thus obtained served as a uniform ellipsoidal polarizing film.

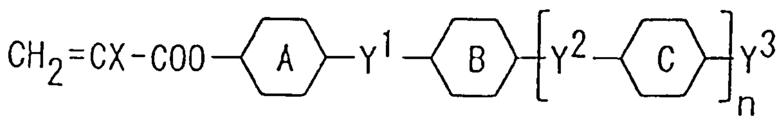
The same STN liquid crystal cell as used in Example 39 was clamped by a polarizing film and the foregoing ellipsoidal polarizing film to prepare a liquid crystal display device. In this arrangement, the angle and position made by the axis of transmission of the polarizing film, the rubbing direction of the glass substrate of the STN liquid crystal cell, and the helical structure of the optically anisotropic film were determined as in the liquid crystal display device of Example 39. When a voltage was applied across the transparent electrodes of the liquid crystal display device, a uniform black-and-white display was provided over a wide range. The liquid crystal display device also exhibited excellent viewing angle properties.

EXAMPLE 41

A polymerizable liquid crystal composition (A-1) made of 85 % by weight of the polymerizable liquid crystal composition (A) obtained in Example 1 and 15 % by weight of a compound represented by formula

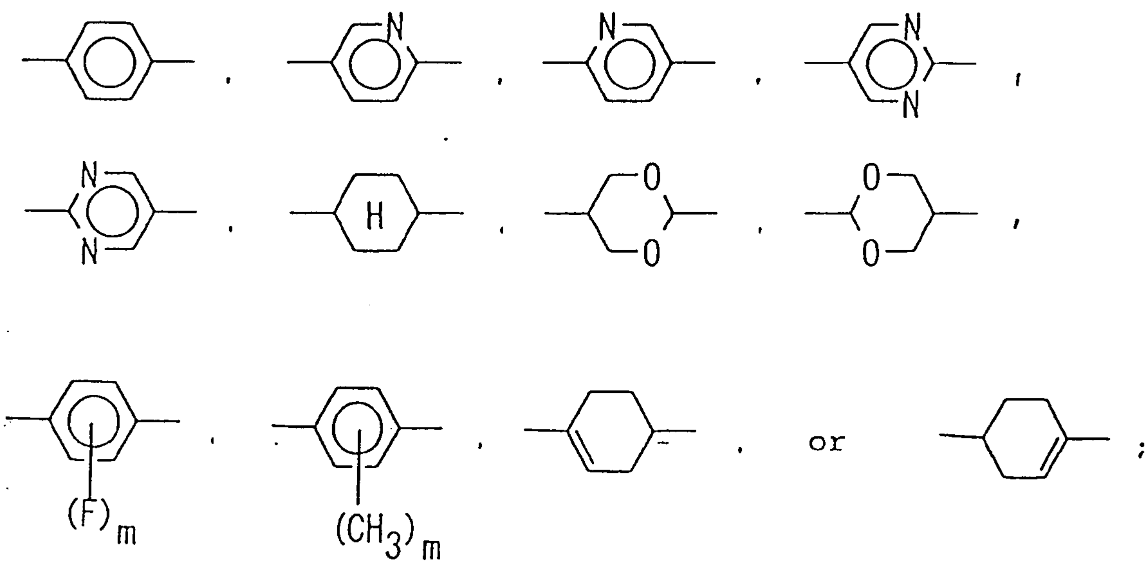
having a liquid crystalline skeleton having at least two 6-membered rings as a partial structure, wherein said composition exhibits a liquid crystalline phase.

2. The polymerizable liquid crystal composition as in Claim 1, wherein said first kind of monofunctional (meth)acrylate compound is a compound represented by the following general formula (I):



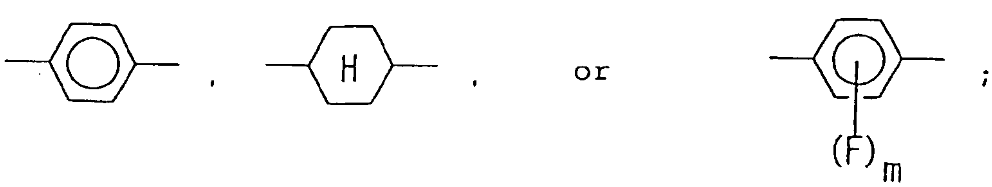
(I)

wherein X represents a hydrogen atom or a methyl group; the 6-membered rings A, B and C each independently represent



n represents an integer 0 or 1; m represents an integer of 1 to 4; Y^1 and Y^2 each independently represent a single bond, $-CH_2CH_2-$, $-CH_2O-$, $-OCH_2-$, -COO-, -OCO-, -C≡C-, -CH=CH-, -CF=CF-, $-(CH_2)_4-$, $-CH_2CH_2CH_2O-$, $-OCH_2CH_2CH_2-$, $-CH=CHCH_2CH_2-$ or $-CH_2CH_2CH=CH-$; and Y^3 represents a hydrogen atom, a halogen atom, a cyano group, a C_{1-20} alkyl group, a C_{1-20} alkoxy group, a C_{1-20} alkenyl group or a C_{1-20} alkenyloxy group.

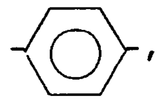
3. The polymerizable liquid crystal composition as in Claim 2, wherein in the general formula (I) the 6-membered rings A, B and C each independently represent



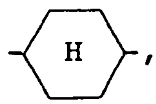
m represents an integer 1 or 2; Y^1 and Y^2 each independently represent a single bond or -C≡C-; and Y^3 represents a halogen atom, a cyano group, a C_{1-20} alkyl group or a C_{1-20} alkoxy group.

4. The polymerizable liquid crystal composition as in Claim 3, wherein in the general formula (I) n represents 0, and Y^3 represents a halogen atom, a cyano group, a C_{1-20} alkyl group or a C_{1-20} alkoxy group.

11. The polymerizable liquid crystal composition as in Claim 10, wherein in the general formula (I) the 6-membered ring A represents

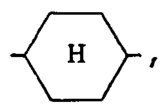


the 6-membered rings B and C each represent

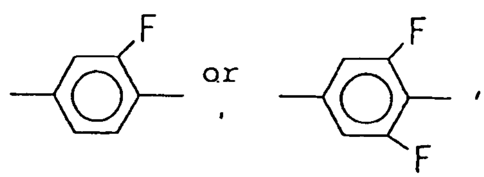


and Y^3 represents a C_{1-10} alkyl group.

12. The polymerizable liquid crystal composition as in Claim 10, wherein in the general formula (I) the 6-membered rings A and B each represent



the 6-membered ring C represents



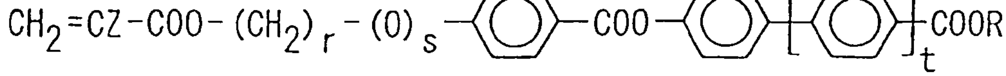
and Y^3 represents a fluorine atom.

13. The polymerizable liquid crystal composition as in Claim 3, wherein said monofunctional (meth)acrylate compound represented by the general formula (I) exhibits a nematic phase.

14. The polymerizable liquid crystal composition as in Claim 1, further comprising a chiral compound.

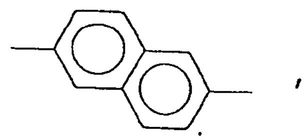
15. The polymerizable liquid crystal composition as in Claim 14, wherein said chiral compound is a (meth)-acrylate compound containing an optically active group and said polymerizable liquid crystal composition exhibits a chiral nematic phase.

16. The polymerizable liquid crystal composition as in Claim 15, wherein said (meth)acrylate compound containing an optically active group is a compound represented by the following general formula (III):

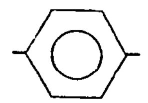


(III)

wherein Z represents a hydrogen atom or a methyl group; s represents an integer of 0 or 1; r



and the other represents



22. An optically anisotropic film comprising a photopolymerization product of a polymerizable liquid crystal composition comprising a first kind of monofunctional (meth)acrylate compound which is a (meth)acrylic ester of a cyclic alcohol, phenol or aromatic hydroxy compound having a liquid crystalline skeleton having at least two 6-membered rings as a partial structure, wherein said composition exhibits a liquid crystalline phase.

23. The optically anisotropic film as in Claim 22, wherein the helix angle due to twisted nematic orientation in said photopolymerization product is in the range of 30° to 360°.

24. The optically anisotropic film as in Claim 23, wherein said optically anisotropic film is a polymerization product of a polymerizable liquid crystal composition which exhibits a chiral nematic phase or cholesteric phase, the structure is fixed in said optically anisotropic film, and the thickness of said optically anisotropic film is greater than the pitch of said polymerizable liquid crystal composition.

25. The optically anisotropic film as in Claim 22, wherein said optically anisotropic film is a polymer obtained by the photopolymerization of a polymerizable liquid crystal composition in a homeotropic alignment, a homogeneous alignment or a hybrid alignment comprising a continuous change from vertical alignment to horizontal alignment in the thickwise direction.

26. The optically anisotropic film as in Claim 22, wherein said optically anisotropic film has partially different optical phase retardation.

27. The optically anisotropic film as in any one of Claims 22 to 26, wherein said optically anisotropic film is supported on or clamped by at least one substrate.

28. The optically anisotropic film as in Claim 27, wherein said substrate has been subjected to rubbing or has an alignment layer.

29. The optically anisotropic film as in Claim 27 or 28, wherein said substrate is selected from the group consisting of a transparent plastic film, a glass substrate and a polarizing film.

30. A liquid crystal display device comprising an optically anisotropic film comprising a photopolymerization product of a polymerizable liquid crystal composition comprising a first kind of monofunctional (meth)acrylate compound as a (meth)acrylic ester of a cyclic alcohol, phenol or aromatic hydroxy compound having a liquid crystalline skeleton having at least two 6-membered rings as a partial structure, said composition exhibiting a liquid crystalline phase.

31. The liquid crystal display device as in Claim 30, wherein said liquid crystal device is of twisted nematic type or supertwisted nematic type.

32. The liquid crystal display device as in Claim 30, wherein said liquid crystal display device is of polymer dispersed liquid crystal type.

Fig. 1

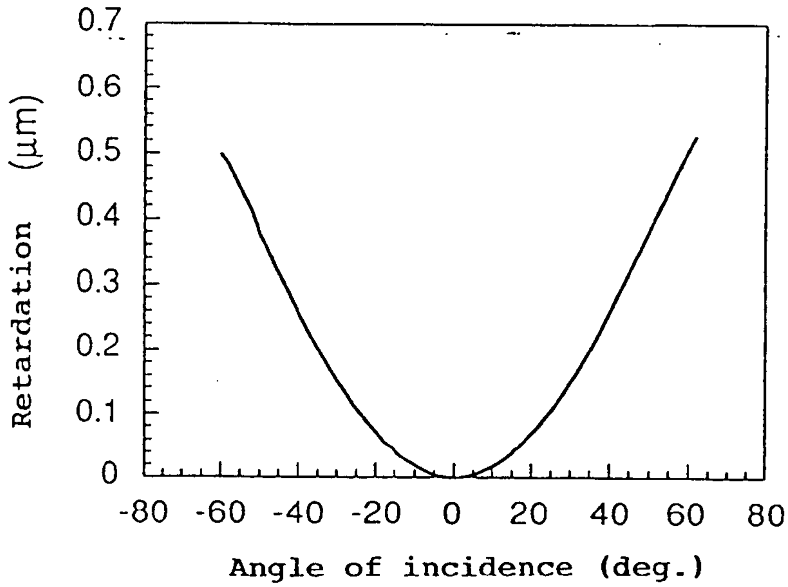

Retardation (μm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-80 -60 -40 -20 0 20 40 60 80
Angle of incidence (deg.)

Fig. 2

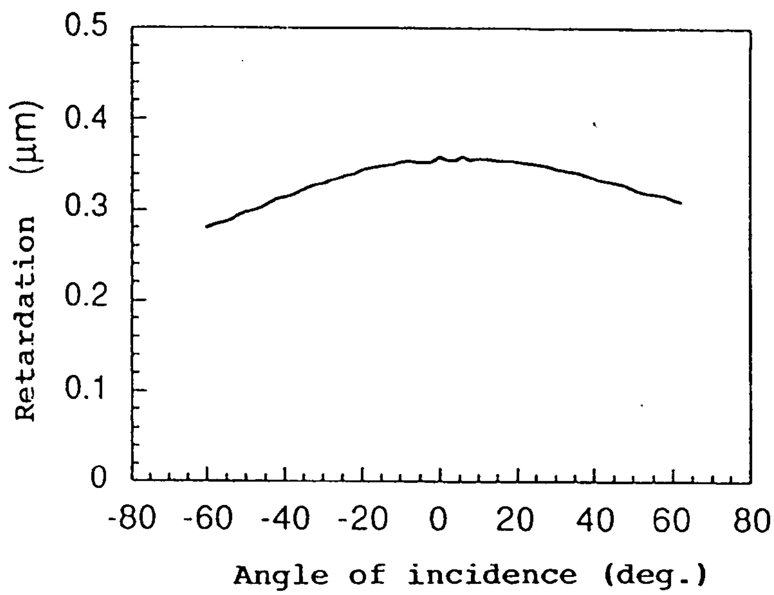

Retardation (μm)
0.5
0.4
0.3
0.2
0.1
0
-80 -60 -40 -20 0 20 40 60 80
Angle of incidence (deg.)

Fig. 4

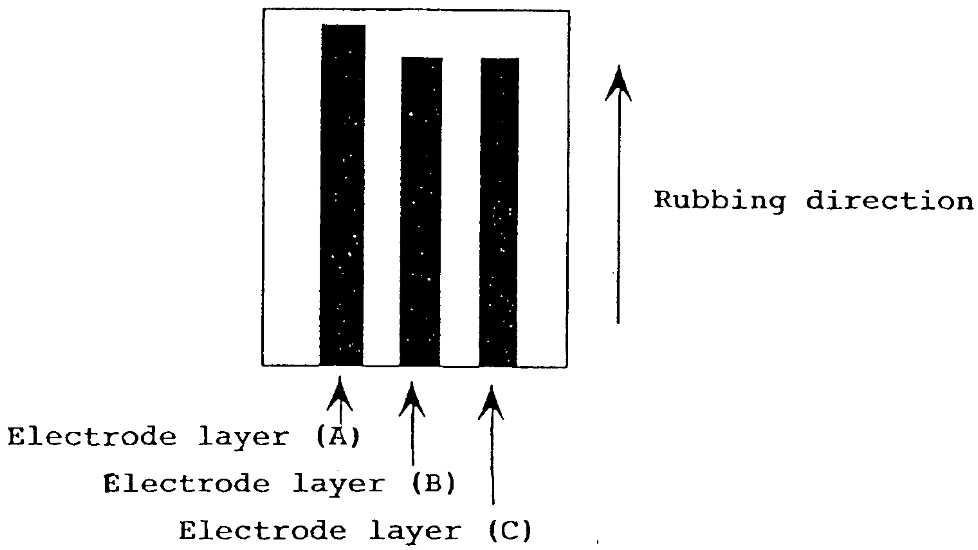

Rubbing direction
Electrode layer (A)
Electrode layer (B)
Electrode layer (C)

Fig. 5

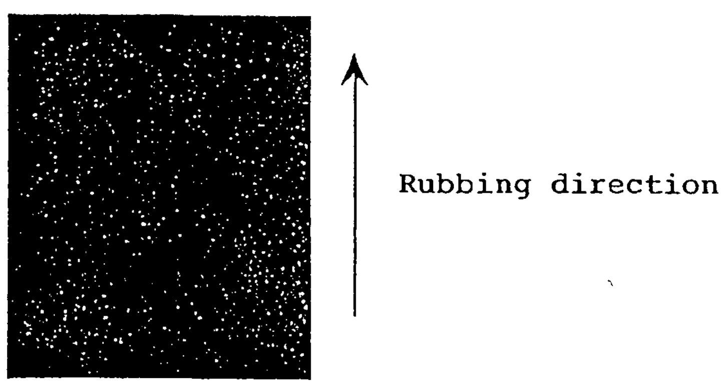

Rubbing direction

Fig. 8

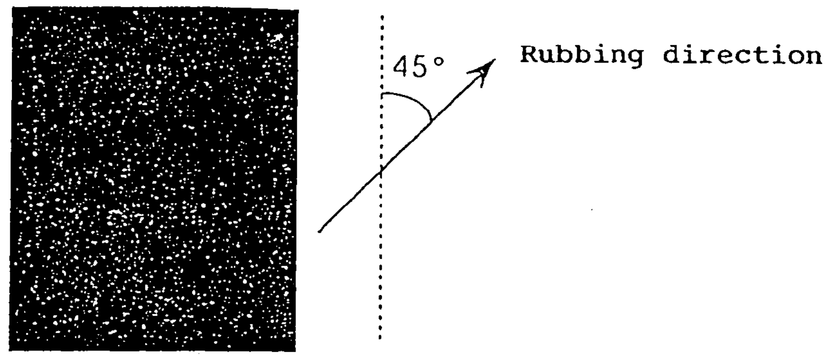
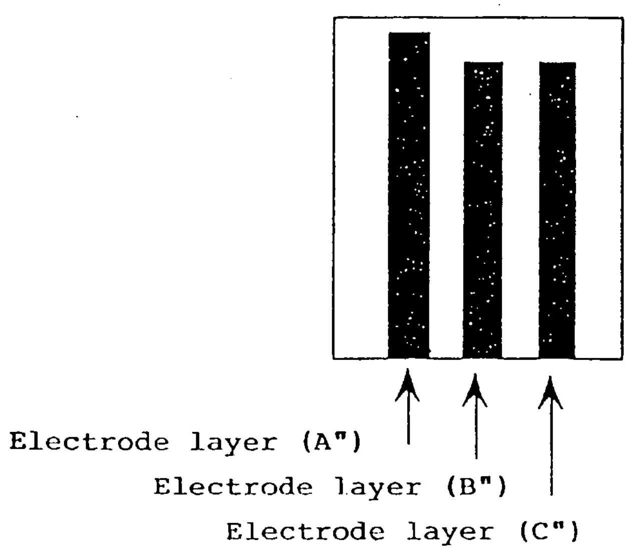

45°
Rubbing direction

Fig. 9


Electrode layer (A")
Electrode layer (B")
Electrode layer (C")

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 12 0614

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	BULL. SOC. CHIM. FRANCE, 1975 pages 2073 - 2076 L. LIÉBERT ET AL. 'polymérisation de monomères mésomorphes initiée par rayonnement ultraviolet'	1,14,15	C09K19/30 C09K19/38 C09K19/12 C09K19/18
A	* the whole document *	2-4,6,13	
X	GB-A-2 002 767 (THOMSON-CSF) * the whole document *	1-4,6,7,13,22	
X	EP-A-0 090 282 (BASF AKTIENGESELLSCHAFT) * claims 1-3,8; examples 2,3 *	1-4,13,30	
X	JOURNAL OF POLYMER SCIENCE, POLYMER LETTERS EDITION, vol.13, 1975 pages 243 - 246 E.PERPLIES ET AL. 'polyreactions in oriented systems, VIII.* polymerization of a liquid crystalline monomer under the influence of a high magnetic field'	1	
A	* the whole document *	2-4,6,13	
X	DE-A-38 37 936 (MERCK PATENT GMBH) * page 9, line 49; table 1 *	1	
A	EP-A-0 563 403 (SEIKO EPSON CORPORATION) * page 11, line 11 - line 17 * * page 19, line 1 - line 9 * * claims 1,2,4,7,9-12,16 *	1-4,6,7	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C09K

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31 March 1995	Puetz, C

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X : particularly relevant if taken alone
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